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14. ABSTRACT University of Maine researchers working in collaboration with Sensor Research & Development Corp. (SRD) have carried out focused research and engineering development towards an advanced hybrid integrated sensor suite for chemical / biological (CB) point detection. The chemical sensor work emphasized the development of new materials and understanding oxide surface chemistry leading to prototype sensing films with specific functionality and interferent class rejection. The biosensor work involved development of acoustic wave and fluorescence-based devices employing immunological and DNA detection probes.				
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FINAL REPORT

“Advanced Development of a Chemical and Biological Sensor Suite”

Grant # N00178-99-1-9002

Project Period: February 10, 1999 -- July 31, 2001

University of Maine

Laboratory for Surface Science & Technology

5764 Sawyer Research Center, Orono, ME 04469

Table of Contents:

1. Overview	1
2. Chemical Agent Sensor Research	3
2.1. Development of a Pre-Processing Stage	3
2.2. Sensor Element Platform Refinement	4
2.3. Semiconducting Metal Oxide (SMO) Film Architectures	6
2.4. Chemical Reaction Mechanisms and SMO Sensor Element Response	9
2.5. Polymer Coated SAW Sensor Elements	13
2.6. Electronics and Data Processing.....	14
3. Biosensor Research	14
3.1. Bulk Acoustic Wave Liquid Phase Devices	14
3.2. Shear Horizontal Acoustic Wave Devices	15
3.3. Silanization Recipes for Biomolecule Attachment	15
3.4. Molecular Beacon and Padlock Probes	16
4. Infrastructure and Instrumentation	17
5. Research Publications and Presentations	17

1. OVERVIEW:

During the terms of this grant (Feb99 – July01), University of Maine researchers in the Laboratory for Surface Science & Technology (LASST) working in collaboration with Sensor Research & Development Corp. (SRD) have carried out focused research and engineering development towards an advanced hybrid integrated sensor suite for chemical / biological (CB) point detection. The hybrid suite is targeted to detect, identify, quantify, and alarm the presence of chemical agents (organophosphorus and chlorinated sulfur compounds), toxic industrial chemicals, and biological agents (pathogenic bacteria and toxins). The requirements for this detector system are low power, high portability, demonstrated sensitivities to sub-lethal doses of the specified agents, and rapid response times that will enable individuals to take lifesaving protective action.

The goals of the University of Maine project have been to carry out the fundamental and applied science that underpins the sensor technologies incorporated into the integrated detector system. This information is input to Sensor Research & Development Corp. whose goal is to perform extensive gas testing and deliver prototype systems that can be tested under live agent scenarios. Efforts at the University of Maine, which encompass both chemical and biological sensing, have focused on the research necessary to develop specific components of the integrated detector system. The chemical sensor work has been the major focus; efforts in the biosensor area were substantially reduced in November 1999 at the request of the Navy to focus more effort on chemical agent detection.

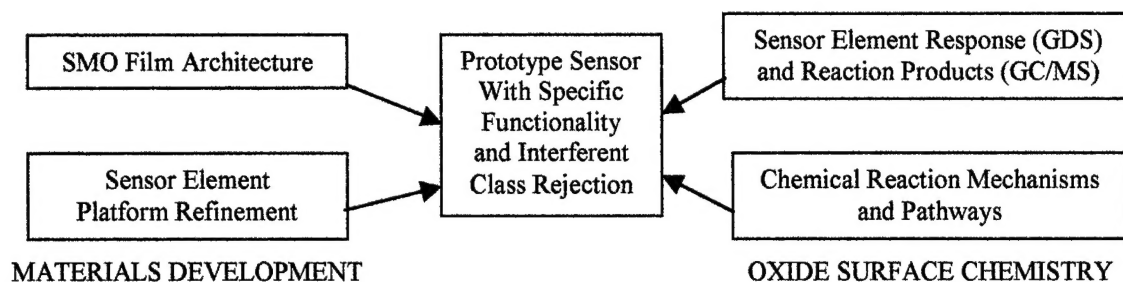


Fig.1 Research efforts for chemical agent sensor.

The chemical sensor work (Fig.1) emphasized the development of new materials and understanding oxide surface chemistry leading to prototype sensing films with specific functionality and interferent class rejection. Extensive laboratory testing has been done to optimize the sensitivity, selectivity and stability of the SMO sensor elements and sensor arrays as a function of gas environments.

Two major problems that received significant attention during the project are *reproducibility* and *selectivity* of SMO films and sensor elements. To attain *reproducibility*, substantial improvements were made in device platforms and film handling (Section 2.2) and SMO film recipes and processing sequences (Section 2.3). Furthermore, accurate calibration and characterization of the gas delivery system (GDS) and associated sensor testing cells was carried out to achieve reproducible sensitivity and response time measurements (Section 2.4). This progress made in obtaining reproducibility was a critical step in being able to make progress in achieving sensor *selectivity*. Experiments focused on selectivity have probed oxide surface chemistry including reactions on SMO films containing metal and metal oxide surface catalysts. Control of surface acidity and subsequent reaction pathways has been shown to be a way to distinguish target and interferent species by their chemical functionalities. Analysis of gas phase reaction products with GC/MS has been used to confirm reaction pathways (Section 2.4)

Major accomplishments in chemical agent sensor research (described in detail in the following sections) include:

- (a) development of a sensor element platform with interdigital electrodes and integral heater that reliably operates at the required device temperature (100 - 500°C).
- (b) recipes for creating reproducible semiconducting metal oxide (SMO) thin films with controlled architecture, including metal and metal oxide catalysts for use as the active sensing element.
- (c) testing of a wide range of sensor elements to several simulant molecules (that mimic functional groups of chemical agents) and interferent molecules using a calibrated gas delivery system (GDS) with integrated gas chromatograph / mass spectrometer (GC/MS).
- (d) determination of chemical reaction mechanisms and pathways on high surface area powders and model sensor surfaces using thermal desorption and optical spectroscopies.

While most of the original concepts and identification strategies for the sensor system were maintained, the design evolved based on modification of the targeted operational specifications and data obtained from research, development and testing. The original configuration called for the integration of two sensor technologies: polymer coated surface acoustic wave devices (SAWs) merged with chemiresistive semiconducting metal oxide sensors (SMOs) into a 'hybrid array'. As schematically shown in Figure 2, the gas stream to be analyzed was to be 'pre-concentrated' to improve sensitivity and 'pre-filtered' to improve selectivity. The "Pre-filtration" aspect evolved into a "Pre-processing" stage where chemical modification of the analyte containing gas stream can be performed. The stream then passes through two

sampling cells placed in series, one containing a set of SAWs and one a set of SMOs. The response signals are 'signal processed' and 'neural networked' to derive the information necessary for agent identification.

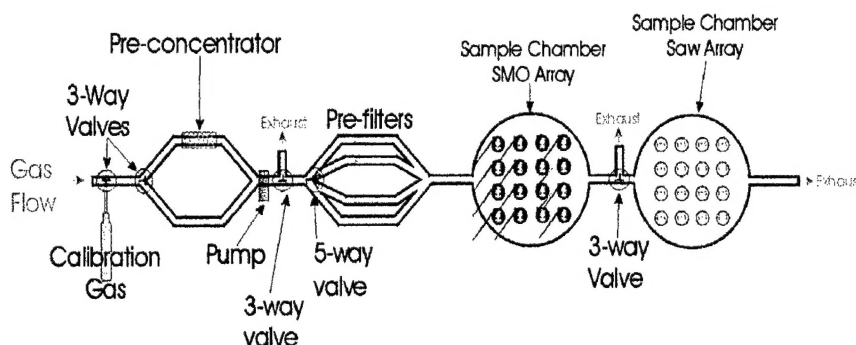


Fig.2 Schematic of prototype hybrid sensor system

The biosensor work (Fig.3) involved development of acoustic wave and fluorescence-based devices employing immunological and DNA detection probes. This work, which is smaller in scope than the chemical detection effort, focused on several aspects of liquid phase detection including sensor device design and testing as well as molecular biochemistry.

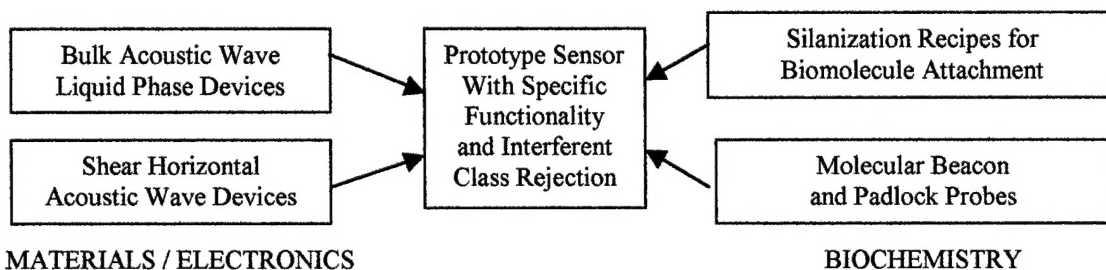


Fig.3 Research efforts for biological agent sensor.

Major accomplishments in biological agent sensor research include the following:

- (a) development of liquid phase bulk acoustic wave and shear horizontal surface acoustic wave sensors including silanization recipes for attachment of biomolecules
- (b) design of fluorescence-based padlock probes and molecular beacons for amplification and detection of specific nucleic acid targets.

2. CHEMICAL AGENT SENSOR RESEARCH

2.1. Development of a Pre-Processing Stage

Present SAW and SMO technologies offer inadequate response selectivity when the chosen analytes consist of complex molecules and gas mixtures. In-line pre-processing of the agent offers great potential in helping to solve this important issue. Viable strategies were developed for the exclusion of a selected group of potential interferents from the analyte containing gas stream and for the chemical modification of analytes to confer reliable *response signatures for identification*.

In-line pre-processing can be performed either within chambers specifically designed for the purpose or on porous films deposited directly on the surface of sensor elements. To evaluate the first approach, a test

device was designed and fabricated allowing precise control of gas flow and temperature with the “processed” gas stream ultimately diverted to an array of sensors and/or a gas chromatography mass spectroscopy system for chemical analysis. Preliminary attempts to deposit porous filters and reactive films directly on the sensor surface were not very successful.

For interferent separation / elimination a variety of protocols have been devised to separate well known “problem compounds” such as methanol, octane, ethanol, and mixtures such as fire retardants and diesel fuel exhaust from a variety of chemical warfare agent simulants. Some of these protocols are based on straight forward approaches such as molecular sizing. Others come from sophisticated chemical analyses. For example, the difference in surface bonding of organophosphonate species on SiO_2 compared to other oxides, as determined by infrared spectroscopy studies, has been used to propose a filtering and preconcentration strategy as shown in Fig.4 for a simulant / interferent mixture of DMMP / methanol. The DMMP is selectively extracted from the gas stream and concentrated on the silica surface, while methanol passes through the filter. The DMMP is selectively adsorbed due to the fact that each DMMP molecule is H-bonded to three surface hydroxyl groups, whereas there is a corresponding 1:1 interaction of the alcohol. Subsequent removal of the concentrated DMMP can be accomplished with a thermal pulse.

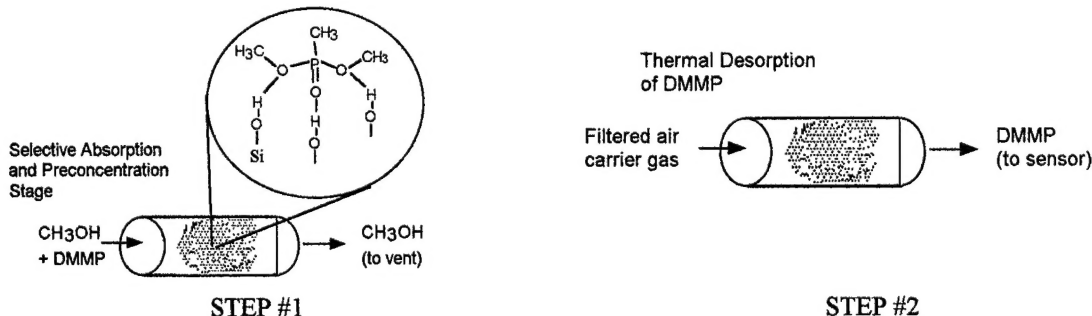


Fig.4 Prefiltration and preconcentration scheme based on the selective adsorption chemistry of DMMP on silica from a mixture of methanol and DMMP. After DMMP selective adsorption at room temperature, heating to 300°C desorbs the DMMP, which can then be delivered to a sensor array.

2.2. Sensor Element Platform Refinement

The sensor platform performance is just as critical as the sensor film element in contributing to sensor reproducibility, long term stability, and overall gas sensor performance. The basic chemiresistive sensor that was developed consists of a sapphire wafer with an electrode pattern covered by an ultra-thin SMO film on the top side and an on-chip heater on the back side (Fig.5). The miniaturization requirement and reduced power of the overall sensor package poses important materials compatibility and temperature uniformity problems. We developed several generations (Figs.6-9) of sensor platforms and solved materials compatibility problems leading to highly reliable sensor elements. This accomplishment was a crucial step in obtaining reproducibility of sensor response. The improvements in the sensor package also allows more rapid testing of sensor films.



Fig.5 Chemiresistive gas sensor device showing the sapphire substrate with SMO film / electrodes on the top side and integrated serpentine heater / resistive temperature device (RTD) on the back side.

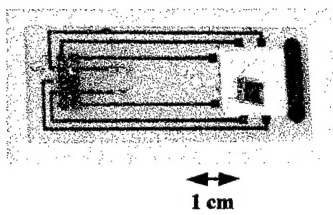


Fig.6 Sensor platform in April 1999. Sensor elements fabricated one-at-a-time and suspended in cutout circuit board by attaching bond wires between sensor and bond pads on board. The board was clamped into a Teflon chamber for gas testing.

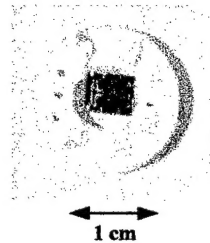


Fig.7 Sensor platform in November 1999. Sensor elements fabricated by double sided wafer batch process, diced, and suspended in Teflon TO-8 style header. These sensors are plugged into test chambers for gas testing.

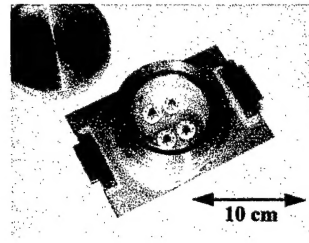


Fig.8 Four sensor elements mounted into pin receptacles of a gas testing cell in November 1999. The circuit board is Ni-plated Teflon with sealed pin receptacles.

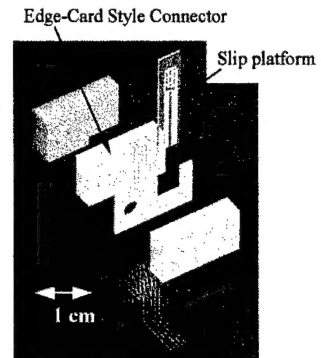


Fig.9 "Slip" sensor platform that plugs directly into the connector package, eliminating the need for wire bonding.

The sensor platform for SMO chemiresistive sensors consists of electrodes upon which the SMO is deposited and on-chip resistive heaters / resistive thermal devices (RTDs) that monitor and maintain uniform temperature during sensor operation. For ultra-thin film SMO sensors, single crystal sapphire (surface roughness < 1 nm) is needed in order to have accurate control of SMO film microstructure. The sensor platform must also be constructed from materials that are compatible with the long term high temperature operating environments (months at 500°C).

Initial wafer batch processing utilized 2" diameter sapphire wafers with 300nm thick Pt electrodes and heaters. A 20nm Ti adhesion layer between the Pt and sapphire was attempted to eliminate delamination at the Pt/sapphire interface. Following post-deposition annealing for 20 hours at 500°C, to stabilize both the RTD performance of the Pt film and the SMO film stoichiometry (baseline conductivity), delamination failure was found to occur during the wire bonding process (Fig.10). This wire bonding failure was found to be due to Ti diffusion into the Pt as determined by scanning Auger analysis (Fig.11). This problem was solved by incorporating a Zr adhesion layer instead of Ti into the process. Bond strength measurements and scanning Auger depth profile results verified that the Zr does not diffuse during the post-deposition anneal or during sensor operation. A new plug-in sensor design which eliminates the need for wire bonding was also developed (Fig.9).

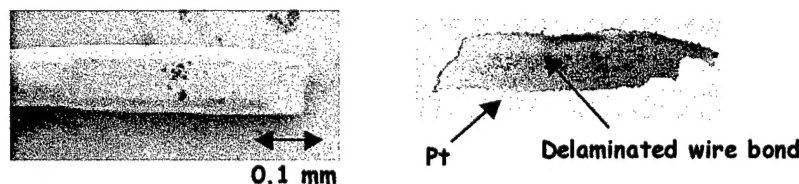


Fig.10 SEM image of a Pt wire bond contacting the Pt bonding pad on the sensor platform. When Ti was used as the adhesion at the Pt/sapphire interface, the wire bonds delaminated following annealing treatments to stabilize the Pt RTD and SMO sensing film. This problem was solved by using a Zr adhesion layer.

Additional wafer process improvements in the microfabrication clean room were required to attain reliable sensor platforms. Important progress included development of a 2-step lift-off photoresist patterning process and elimination of a Au layer used during two-sided patterning to reduce UV bleedthrough during pattern development. The wafer fabrication process was extended to 3" sapphire wafers in April 2000 to yield ~90 die per wafer (6 mm devices). A new mask was designed with 3.25

mm devices containing a variety of electrode geometries and heater designs (~300 die per wafer) in May 2000 and successful production of 3 mm sensors was achieved in July 2000 (Fig.12). The current platform microfabrication process requires 116 steps to produce each wafer. Accelerated failure tests of temperature cycling from 80°C to 420°C shows no failure after at least 18,000 cycles. Failure due to delamination occurs only at temperatures exceeding ~830°C.

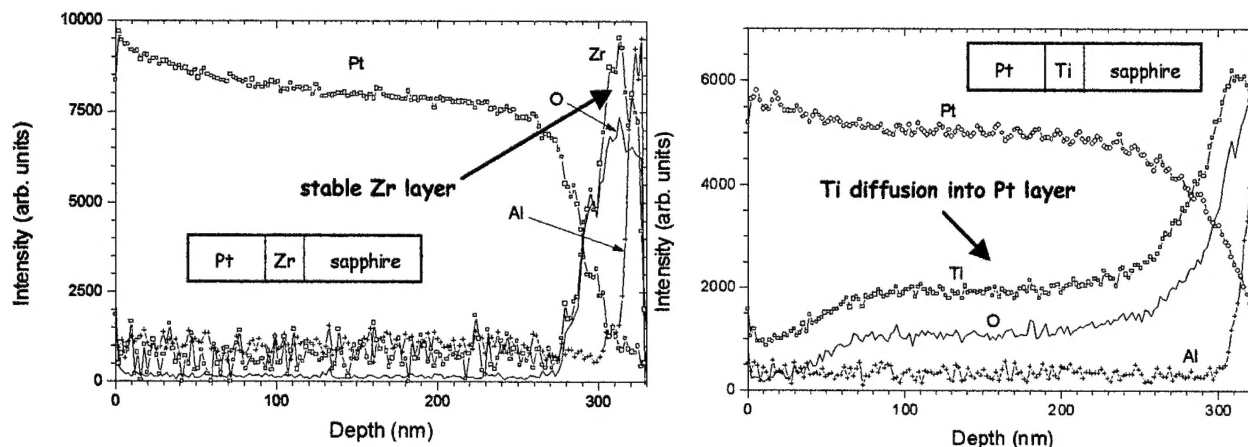


Fig.11 Auger spectroscopy depth profiles of Pt/Zr/sapphire (left) and Pt/Ti/sapphire (right) samples after post-deposition annealing treatment showing that Ti diffuses into the Pt film while the Zr is immobile. The depth scale increases from the top Pt surface (0 nm) to the Zr/sapphire or Ti/sapphire interface (320 nm) .

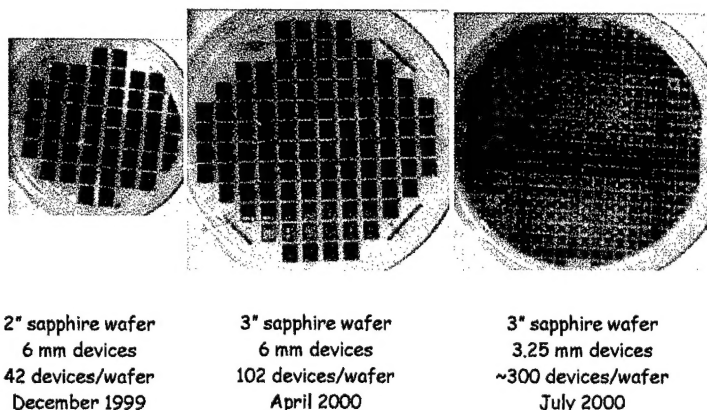


Fig.12 Photographs showing the evolution of sapphire wafers containing chemiresistive sensors that were fabricated in the LASST clean room.

2.3 Semiconducting Metal Oxide (SMO) Film Architectures

The SMO film is the critical component that provides the sensitivity and selectivity of the sensor element. We developed deposition recipes to produce ultra-thin (<100nm) WO_3 films either in pure form or containing metal (Au, Ag) or metal oxide (TiO_2 , SnO_2 , CuO , $\text{In}_2\text{O}_3/\text{SnO}_2$, GaO_2 , SiO_2) surface catalysts. The thin film synthesis and processing facility at LASST allows for precise control of film deposition parameters under ultra-high vacuum conditions. Processes were first developed to achieve film reproducibility, which was a prerequisite to our further work that has explored the phase fields / microstructure as a function of deposition parameters and processing treatments.

A major accomplishment was the achievement of reproducible film microstructures (as measured by RHEED, XRD, AFM analysis) and stoichiometries (as measured by XPS, AES, Raman analysis). The

reproducibility was also verified by conductivity sensor measurements (see Section 2.4). Fig.13 shows two pure WO_3 microstructures on r-cut sapphire which can be routinely produced, an epitaxial monoclinic phase grown at 650°C and an epitaxial tetragonal phase grown at 450°C . These highly oriented “epitaxial” WO_3 films are very stable with post-deposition annealing; for example, the full-width-half-max (FWHM) of the XRD peaks, which is a function of strain and grain size, does not change within the measurement accuracy after a 20 hour 450°C anneal in air (above typical sensor operating temperatures). These films also yield very reproducible baseline conductivities on the sapphire sensor element platforms.

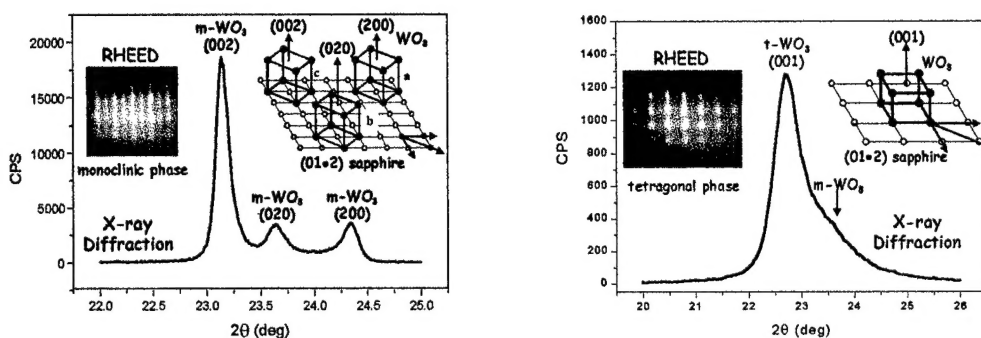


Fig.13 Different WO_3 film microstructures produced by varying temperature during magnetron sputter deposition. Reflection high energy electron diffraction (RHEED) and x-ray diffraction (XRD) measurements indicate the crystalline phase, orientation, and crystal quality. Monoclinic phase WO_3 (left) is formed at 650°C and tetragonal phase WO_3 (right) is formed at 450°C deposition temperature.

Small deviations in SMO film stoichiometry yield oxygen vacancies that donate electron carriers into the conduction band. The precise WO_{3-x} stoichiometry of the as-deposited films is a function of the gas composition in the magnetron sputtering plasma. Fig.14 shows XPS results indicating a 30% O_2 threshold required to obtain the nominal WO_3 composition. *In situ* conductivity measurements of films deposited over a range of O_2/Ar ratios above this threshold (Fig.15) show that the film conductivity can still vary over 8 orders of magnitude as a consequence of subtle changes in vacancy concentration. Post-deposition annealing treatments were found to be necessary to attain a reproducible and stable baseline conductivity. For example, annealing at 400°C in air for 12 hours equilibrates the film with a known vacancy concentration independent of the starting stoichiometry (Fig.15). The baseline conductivity is dictated by the exact temperature and oxygen partial pressure in the annealing environment. Thus, we have found that post-deposition annealing conditions can be tailored to yield a stable baseline conductivity for a specific sensor operating temperature.

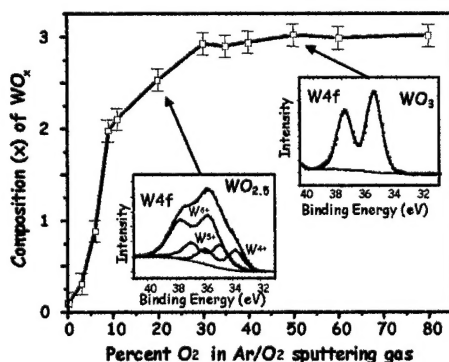


Fig.14 Stoichiometry of WO_x films as a function of the Ar/O_2 ratio in the sputtering gas as measured by x-ray photoelectron spectroscopy (XPS). The insets show spectra of the W4f energy level which indicate the local charge state on the tungsten cations.

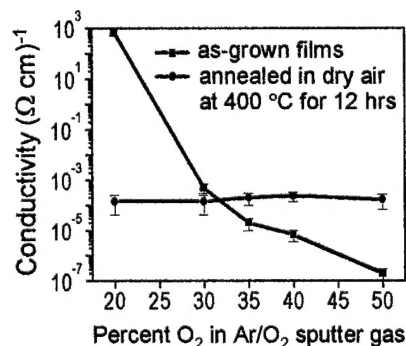


Fig.15 Conductivity of WO_{3-x} films, measured under ultra-high vacuum immediately after deposition, varies over 8 orders of magnitude depending on the O_2 content in the sputter gas. The baseline conductivity is stabilized by post-deposition annealing.

Other WO_3 film microstructures were produced by changing parameters including sputtering power, sputter gas content, deposition rate, and temperature. Fig.16 shows XRD profiles from films having either epitaxial, highly oriented, or random polycrystalline structure. Post-deposition annealing studies using XRD show that for both polycrystalline and highly oriented films, structural changes do occur during annealing and these changes are difficult to control in a reproducible manner. The epitaxial films, however, exhibit a microstructure that remains unchanged from the as-deposited state following long term annealing up to 500°C . Based on these results, we chose the epitaxial films as the standard films for gas sensor testing since they are best suited for stable sensor performance. The epitaxial microstructure also provides a reproducible surface for studies of catalytic additives.

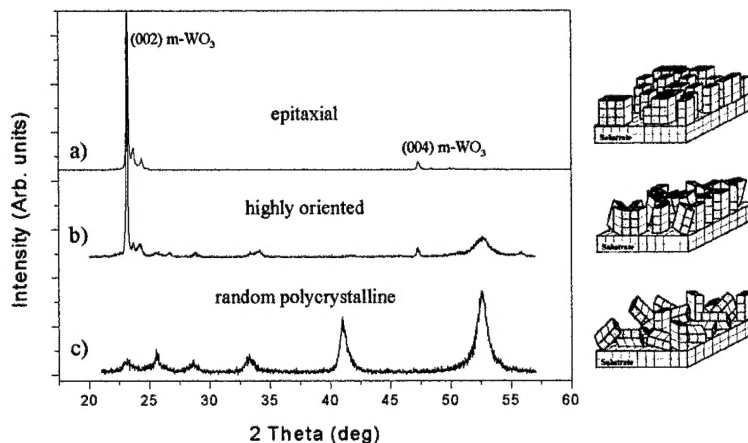


Fig.16 X-ray diffraction (XRD) spectra showing three types of WO_3 film microstructures (a) epitaxial monoclinic phase grown at 650°C ; (b) highly oriented grain structure formed by 30°C deposition followed by 90 min 600°C anneal in 10^{-4} torr O_2 and 20 hour 450°C anneal in air; and (c) random polycrystalline structure formed by 200°C deposition followed by 20 hour 450°C anneal in air.

Both metal and metal oxide catalyst particles were deposited on WO_3 films as a means to explore film selectivity to specific target gases during sensor element testing (Section 2.4). To be effective, the catalysts must be highly dispersed particles (high surface area) on the SMO surface. The materials challenge is to stabilize the size of the nanosized particles, which coalesce and coarsen at typical sensor operating temperatures (300 – 600°C). Scanning electron microscopy images in Fig.17 show the coarsening of Au particles on a WO_3 film surface as a function of annealing time. Analysis of particle size distributions indicated that the aggregation mechanism is via island mobility rather than individual atom surface diffusion. These microstructural changes may have a significant influence on sensor response and long term reproducibility. WO_3 sensors fabricated with metal oxide catalysts provides an alternative SMO modification to achieve gas selectivity. The influence of these catalysts on sensor response have been measured (Section 2.4) but the metal oxide catalyst dispersion and stability has not yet been determined.

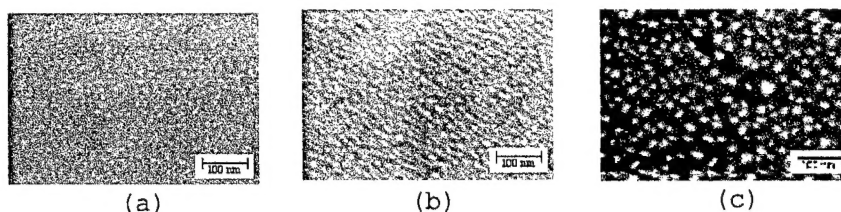


Fig.17 SEM images of dispersed Au catalytic particles (3.2 nm equivalent thickness) on a WO_3 surface showing particle size coarsening at typical sensor operating temperatures (a) after 3 hours at 400°C (b) after additional 13 hours at 400°C (c) after additional 7 hours at 600°C .

2.4 Chemical Reaction Mechanisms and SMO Sensor Element Response

Manipulation and understanding of oxide surface chemistry is critical to the development of selective SMO sensor elements. The chemisorption and reaction of organophosphonate compounds with WO_3 -based materials were studied using spectroscopic techniques (infra-red adsorption, thermal desorption, gas chromatography, mass spectroscopy) to determine the sensing mechanism and provide ways to improve the selectivity of a sensor array. From studies of the reaction mechanism, we determined certain constraints on the information which can be obtained from the time-varying conductivity signal of SMO sensor elements. These constraints and differences in reactivity toward target compounds were used to select optimum sensor array elements. The spectroscopic studies have been correlated with gas testing results performed on a variety of SMO sensor elements.

SMO gas sensors operate in a mode in which a hydrocarbon (target gas) is oxidized (burned) at a rate determined by the chemical reaction kinetics. Reduction of the oxide or reaction of chemisorbed oxygen ions, such as O^- , increases the mobile electron carrier concentration, which is detected as a change in conductivity. When operated in air, oxygen and water reoxidize the surface and restore the sensor to its original conductivity when the target gas is removed. Therefore, the conductivity is controlled by the rates of competing oxidation and reduction reactions, as illustrated in Fig. 19.

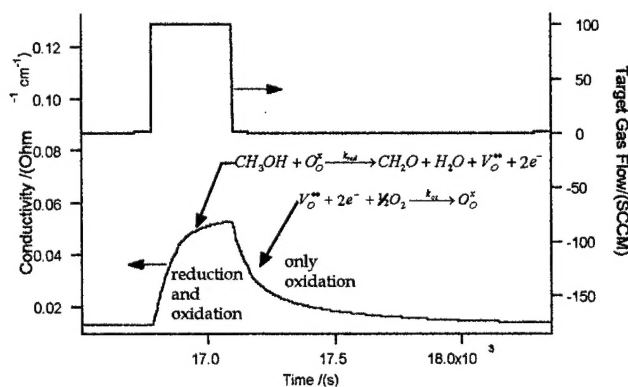


Fig. 19 Schematic illustration of competing reactions during response of a WO_3 sensor to methanol.

Our experiments showed that the reaction rate is a function of the target gas concentration, surface temperature, acid and base characteristics of the oxide (Lewis and Brønsted), coverage of oxygen ions, and the ease with which the oxide can be reduced (related to the heat of formation of the oxide). The sensitivity depends upon the stoichiometry of the redox reaction, as well as the reaction probability for an incident molecule, which involves sticking coefficients and surface residence times. The remainder of this section discusses the results of experiments that have probed these issues in detail.

Fig. 20 shows the chemical structure of organophosphonate compounds used as simulants for the live agents. A common feature of the nerve agents is the alkoxy groups, which may be oxidized on SMO films. Therefore, we have focused on the reaction pathways of the methyl and methoxy groups in the organophosphonates and the fate of the phosphate backbone.

Infrared adsorption studies that identify the vibrational modes of adsorbed molecules and surface intermediates were carried out to investigate the interaction of these compounds with WO_3 surfaces. To increase the signal intensity from the adsorbates, measurements were performed on high surface area powders and then correlated with reactions on WO_3 thin film surfaces. Commercial WO_3 particles proved unsatisfactory for these infrared studies because the large particle size (20 microns) led to unacceptable levels of light scattering. Thus, we developed a sol-gel synthesis recipe to produce particles of order 0.4 micron diameter which both lowered scattering levels and provided higher surface area.

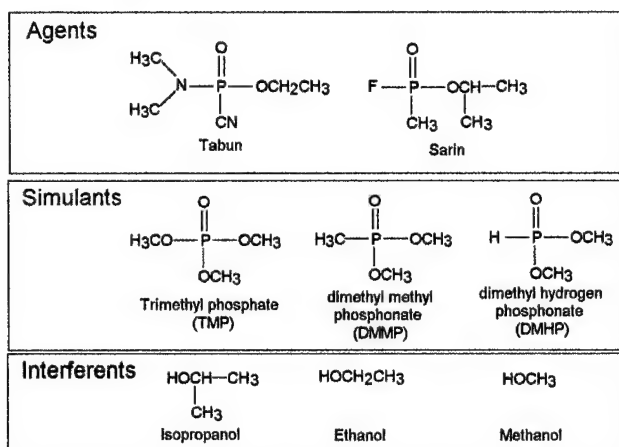


Fig.20 Chemical structure of chemical warfare agents, organophosphonate compounds (simulants), and common interferents.

Adsorption of DMMP on other oxides (*prior to our work, no results in the literature had been reported for WO₃*) has been suggested by Weinberg's group at Cal Tech to occur through the phosphoryl oxygen directly with a Lewis acid site. Our results on both highly dispersed WO₃ particles as well as TiO₂ powders indicate that the interaction is clearly associated with isolated surface hydroxyl groups, as shown in Fig.21. Transmission infrared studies on highly dispersed WO₃ particles as well as TiO₂ powders show that DMMP, DMHP, and TMP adsorb molecularly at room temperature. The shift in the P=O stretch, relative to gas phase frequencies, indicates that the phosphoryl group is involved in chemisorption.

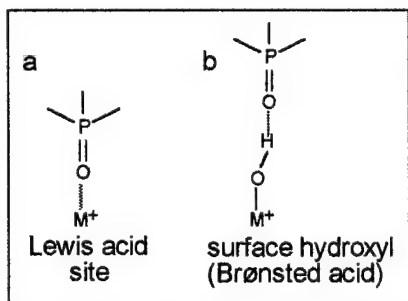


Fig.21 Initial chemisorption interaction of DMMP with an SMO surface (a) suggested by Weinberg and (b) our proposed structure.

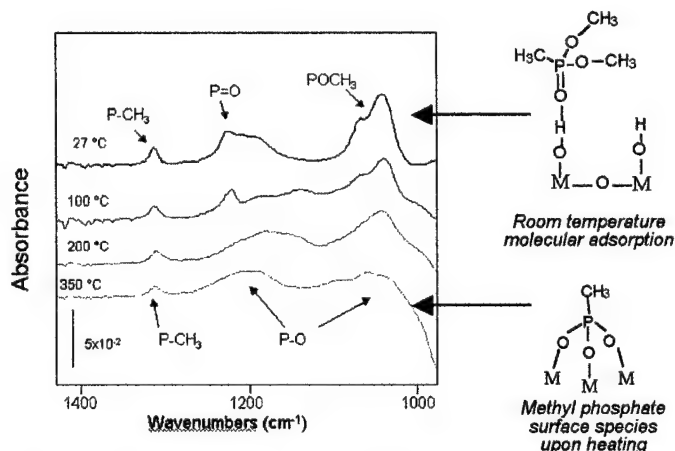


Fig.22 Infrared spectra of DMMP after adsorption on WO₃ powder at room temperature. The infrared absorbance peaks are associated with vibrational features of the P=O group interaction on the surface as well as CH₃, CH₃O, and P-CH₃ vibrational modes of the chemisorbed molecules.

The presence of surface hydroxyls in our experiments was found to be critical to the decomposition of DMMP at higher surface temperatures, which is directly related to the effect of humidity on sensor response. Surface hydroxyl groups present at room temperature cause DMMP to decompose on WO₃ upon heating via loss of the methoxy groups, but the methyl group remains (Fig.22). Infrared absorbance features acquired after heating above 300 °C contain -PO₃ stretching modes indicating the formation of methyl phosphate-like species.

Adsorption of DMMP on SiO_2 was found to be markedly different from the adsorption of DMMP on WO_3 , TiO_2 , and Al_2O_3 . While decomposition of DMMP occurs with loss of methoxy groups after heating above 300°C on the latter oxides, on high surface area SiO_2 powders only molecular adsorption and desorption is found. DMMP adsorbs via the P=O and the two methoxy groups on silica and completely desorbs from the surface upon heating (Fig.23). The infrared spectra for adsorption on silica show no reduction in the number of hydroxyl groups and there was no evidence of any adsorbed methyl phosphate or other species. This difference in surface bonding between SiO_2 and the other oxides is the basis of the filtering and preconcentration strategy discussed in Section 2.1.

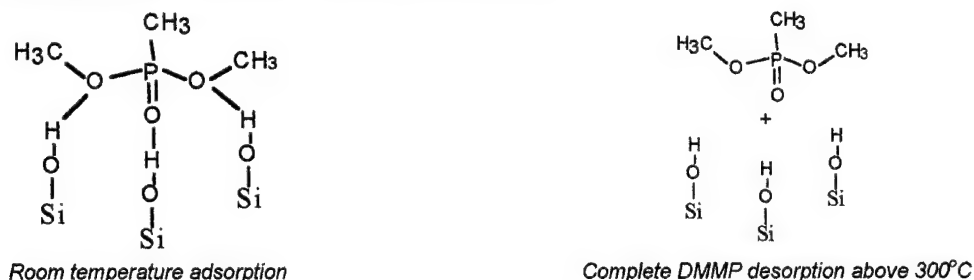


Fig. 23 Adsorbed species on a SiO_2 surface following exposure to DMMP

In general, the reaction of DMMP with the surfaces of metal oxides leads to several reaction products depending on the exact reaction conditions. However, only those reaction pathways which create a change in electron carrier concentration cause a response for the chemiresistive sensor. Fig.24 illustrates several reaction product possibilities. An interaction with a surface hydroxyl group (Brønsted acid) or with water (via condensation of hydroxyls) leads to methanol, with negligible change in carrier concentration. On surfaces such as TiO_2 , in which O^- species are thought to be stable at working temperatures, complete combustion occurs. At higher temperatures and on oxides with more highly charged cations, such as WO_3 , O^- species are known to be less stable and reaction with lattice oxygen leads to selective oxidation products. Furthermore, the reaction of methanol in air on WO_3 catalysts at $200\text{--}400^\circ\text{C}$ leads to formaldehyde, via a methoxy intermediate. The rate limiting step in this case is the α -H abstraction and the hydrogen combines with lattice oxygen to desorb as H_2O . Both formaldehyde and CO_2 production are redox reactions, which increase the conductivity of the oxide. Which of these reaction pathways become operative can be controlled by manipulating the surface acidity and choice of semiconducting metal oxide.

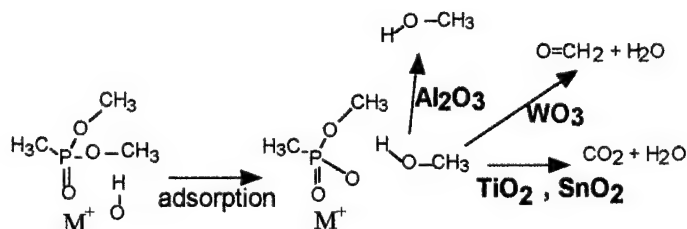


Fig.24 Possible reaction pathways and products for the reaction of the methoxy group of DMMP.

To exploit these differences in surface chemistry for the different oxides to achieve improved gas selectivity, we fabricated and tested many sensing films that consisted of an epitaxial WO_3 microstructure covered by monolayer amounts of one of five different oxide additives (SnO_2 , InSnO_2 , TiO_2 , SiO_2 , CuO) which differ in Lewis and Brønsted acidity, metal-oxygen bond strength, and carrier type (n vs. p). The results indicate that the sensitivity varies dramatically over three orders of magnitude. Fig.25 illustrates the dynamic range of the change in conductivity for exposure of these sensors to DMMP at the same concentration and several temperatures. The behavior found in several different batches of sensors

indicated that WO_3 sensors modified with SnO_2 and TiO_2 were typically 100 times more sensitive than pure WO_3 , and SiO_2 modified sensors were about a factor of 10 less sensitive.

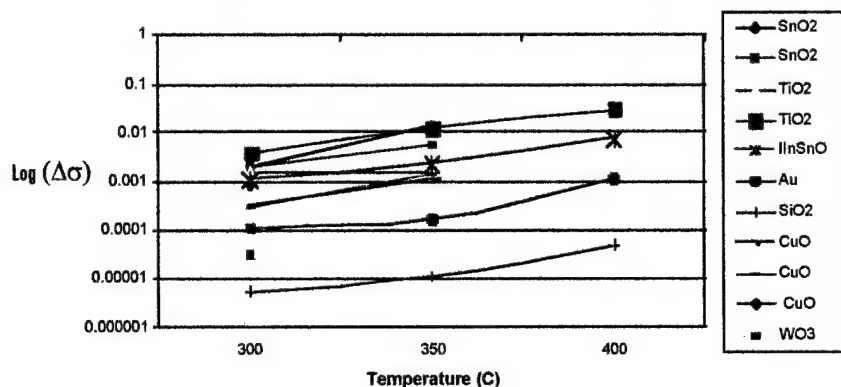


Fig.25 Sensor response ($\Delta\sigma$) to 1 ppm DMMP at several temperatures showing a variation by over 3 orders of magnitude. Repetitive tests with an automated gas delivery system showed the same pattern of reactivity and similar dynamic range. The sensor reproducibility, as measured by dividing the standard deviation of the three responses at a given concentration and temperature by the average sensor response, averaged 14% at all three temperatures. Improvements in the sensor platform have led to a decrease in this figure to 5-10%.

Experiments to study reaction pathways on WO_3 surfaces were carried out in which the product distribution from thermal desorption studies in vacuum were correlated with GC/MS measurements from sensors operating under ambient conditions. Under vacuum conditions, DMMP reacts with the clean WO_3 surface to produce fragments at 31 amu (methanol), 30 amu (formaldehyde), and 46 amu (dimethyl ether). Quantitative determination of these products and reaction rates are complicated by the presence of exposed Pt electrodes and a hot sapphire substrate on the sensor platform.

The decomposition of DMMP to form formaldehyde can be considered as a two step process (Fig.26). If the first step (decomposition of the organophosphonate molecule) is the rate determining step, then the magnitude of the sensor response may be sensitive to differences in the stability of the various organophosphonates. By contrast, if the second step is the rate determining step then the response to methoxy intermediates created from decomposition of organophosphonates may not be significantly different from methoxy intermediates formed from exposure to methanol. In such a case, methanol would be a strong interferent and would have to be removed from the gas stream by pre-filtration. Under some conditions, we have found that the response curves of a WO_3 sensor to DMMP and methanol are essentially indistinguishable (Fig 27).

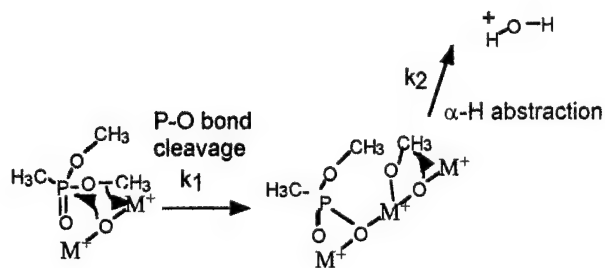


Fig.26 Decomposition of DMMP on WO_3 shown as a two step process: methoxy intermediate formation followed by formaldehyde desorption.

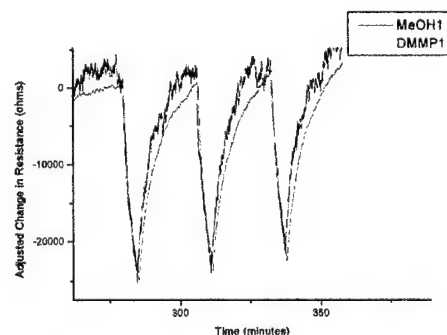


Fig.27 Sensor response to DMMP vs. methanol show similar time dependence suggesting that the rate limiting step is the same.

Examination of the structure of the live agents, Sarin and Tabun (Fig.20), shows that these molecules contain ethoxy and isopropoxy groups, respectively, which may have significantly different rates of reaction than the methoxy functionality of DMMP. Because ethanol and isopropanol may react similarly to Sarin and Tabun, respectively, the simple alcohols are all potentially deleterious interferents to the SMO sensor. However, if the alcohols can be removed (e.g. by SiO_2 pre-filtration, Fig.4) then differences in the rates of the ethoxy and isopropoxy intermediates (formed during decomposition of Sarin and Tabun) may lead to more specific discrimination between organophosphonates. The generality of this proposed reaction sequence remains to be determined.

Build-up of phosphate intermediates leads to “poisoning” of SMO sensor elements. As stable phosphate species form, they block surface sites and cause irreversible changes in the sensor conductivity. We have tried to exploit this sensor poisoning as a means of identifying the presence of organophosphonates. Thermal desorption spectra from a WO_3 surface as a function of dose to DMMP (Fig.28) show that the decomposition process for DMMP on the clean surface becomes poisoned and only molecular adsorption and desorption can occur once stable phosphate species are formed. This same effect is visible in sensor gas response data (Fig.29); the conductivity change after sequential gas pulses does not recover to the pre-exposure baseline. Experiments involving O_2 and N_2 exposure of the poisoned surface indicate that these probe molecules are good indicators of sensor activity and may provide another sensing approach to signal poisoning by organophosphonate exposure.

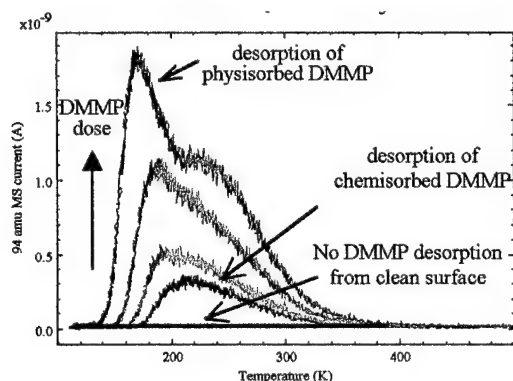


Fig.28 Thermal desorption of molecular DMMP from a “poisoned” WO_3 surface following repetitive DMMP exposure and thermal cycling.

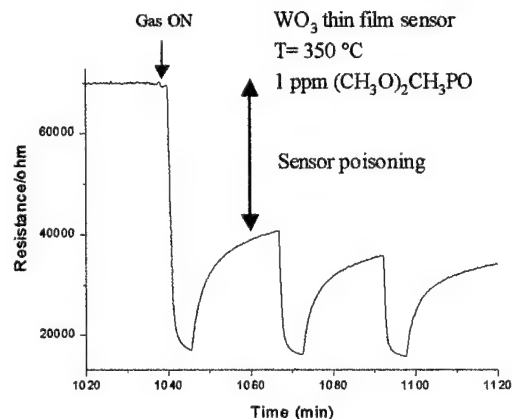


Fig.29 Response of WO_3 sensor to 1 ppm DMMP exposure showing poisoning effects with repetitive gas exposure.

Another aspect of the conductivity vs. time plot which seems to correlate with exposure to organophosphonates is the time constant associated with the recovery. The reoxidation reaction in selective oxidation catalysts follows a pseudo-first order rate law, and thus a combination of the time constant and irreversible changes in conductivity may be exploited to identify the presence of organophosphonates. The steady state concentration of vacancies within the SMO film should be related to the total concentration of reducing gases present and, in principle, may be used to quantify the gas concentration. Further studies, particularly with mixtures of simulants and interferents, need to be done to assess the practical limitations of this approach.

2.5 Polymer Coated SAW Sensor Elements

The fabrication of SAW sensor elements possessing modest selectivity was performed by applying polymers modified with a variety of functional groups to an acoustic wave platform surface. As with SMO elements, complex molecules do not provide definitive response profiles. Arrays of polymer coated SAW devices were tested in parallel with the SMO sensors to examine response to breakdown products and derivatives. Attempts were made to use molecular imprinting to achieve a very high degree of

selectivity to SAW arrays. The SAW sensor were primarily a development effort since most of the research has been done by groups at Naval Research Laboratory and elsewhere.

2.6 Electronics and Data Processing

All of the circuitry developed and fabricated to allow high throughput testing of sensor elements was designed to be easily adapted for service in final prototype instruments. The electronics allows independent regulation of the heating profiles for 10 sensor elements. 'Auto-ranging' electronics has also been built to allow simultaneous DC resistance measurements of 10 individual sensors. A first generation system involving PIC chips capable of control of both the heater and resistance measurement circuits was also developed. High frequency oscillators have been designed and fabricated for SAW elements. All of these can be scaled up to accommodate an array incorporating as many sensor elements as will be ultimately necessary.

The ultimate instrument must have the capability to provide some quantitative estimate of analyte concentration. A variety of system solutions to this problem (calibration protocols, sequential activation of sensors, etc.) were attempted both in the realm of computer modeling and with directed bench experimentation. Of particular concern is the ability of the instrument to chart changing concentrations of analytes. Improvement in the design of SMO elements has allowed reasonable approaches to these issues. In addition, a variety of signal processing paradigms have been studied to continually assess sensor element needs and to help determine the requirements for a microprocessor for the ultimate prototype design.

3. BIOSENSOR RESEARCH

3.1 Bulk Acoustic Wave Liquid Phase Devices

The bulk acoustic wave (BAW) resonant sensor, which utilizes the thickness shear mode (TSM) in AT-cut quartz, has been widely used for liquid phase biosensing applications. However, the conventional BAW sensor geometry does not allow the penetration of the electric field associated with the TSM into the liquid, and results in a sensor response which is only related to the change of the liquid mechanical properties. In the present work, a variety of BAW sensors with different sensing electrode configurations have been fabricated and tested in saline solutions (Fig.30). The results show that the sensitivity (changes of the liquid electrical properties) increases when the overlap area between the two electrodes of the

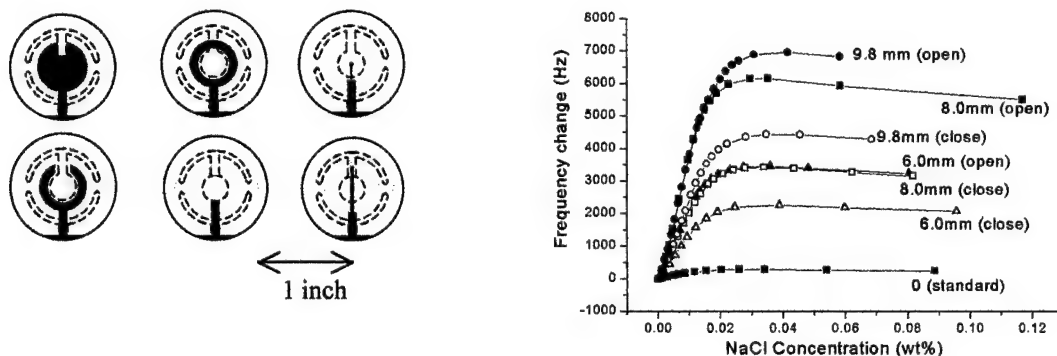


Fig.30 Various electrode configurations (left) for bulk acoustic wave sensors which allow the electric field of the excited mode to penetrate into the liquid. Measured frequency changes (right) as a function of the NaCl concentration in the liquid making contact with the sensor surface.

sensor decreases, and can be more than 25 times larger than that obtained by a standard BAW sensor. A new equivalent circuit model has been developed and the impedance calculated from the model agrees very closely with the measured impedance. The liquid in contact with the sensor forms a “lossy electrode” on the sensing surface, which enables an efficient excitation of the thickness shear mode to occur. The novel geometries developed in this project can be tested as a new class of BAW liquid phase sensors, which will be more than an order of magnitude more sensitive than the standard BAW sensor.

3.2 Shear Horizontal Acoustic Wave Devices

The Bleustein-Gulyaev (BG) wave is one of the most exciting acoustic waves for fluid phase biosensing applications since this wave is a pure shear horizontal (SH) SAW, which has a single displacement component transverse to the propagation direction and an electric potential. It does not radiate energy into the fluid and is capable of detecting subtle mechanical and electrical property changes in the fluid. Potassium niobate is one material in which BG waves can be efficiently generated. We performed theoretical calculations of the SAW velocities and the associated mechanical and electric field quantities (Fig.31) for many crystallographic orientations of potassium niobate (KNbO_3). The calculations show that the entire Z-axis cylinder family of cuts belong to the “four row two zero” case, and is capable of supporting BG waves. The coupling coefficient ranges from a minimum of 1.28 percent at 90 degrees to a maximum of 53 percent at 0 degrees, which is significantly larger than any coupling coefficient observed in quartz that has been used in liquid phase sensing applications. One of the elastic constants in KNbO_3 has a positive temperature derivative, which suggests KNbO_3 may possess temperature compensated cuts. Experimental characterization of the BG wave propagation properties in KNbO_3 was performed including mask design, device fabrication and microwave measurements. Attachment of biomolecules to the KNbO_3 surface was carried out and initial results demonstrate its feasibility as a highly sensitive liquid phase acoustic wave sensor.

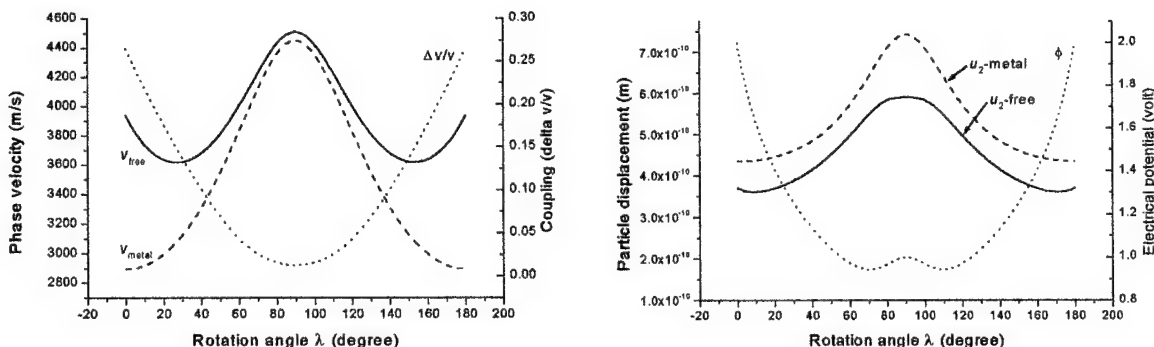


Fig.31 SAW velocities, piezoelectric coupling efficiency, lattice displacement, and electric potential calculated as a function of crystallographic orientation for a potassium niobate crystal. These values are substantially better than for traditional piezoelectric crystals such as quartz.

3.3 Silanization Recipes for Biomolecule Attachment

The development of effective attachment protocols of biomolecules to surfaces is a critical step in biosensor production. Our work centered on the use of aminosilanes since these linker molecules are bifunctional containing a reactive group that covalently binds to the surface and a second bioreactive functionality (NH_2 or COOH) that extends from the surface (Fig.32). A major portion of this aminosilane research focused on controlling the day-to-day variance in the nature of the attached species to the biosensor surface. The base-catalyzed gas phase reaction process that we developed eliminates irreproducibility and leads to well-defined coatings.

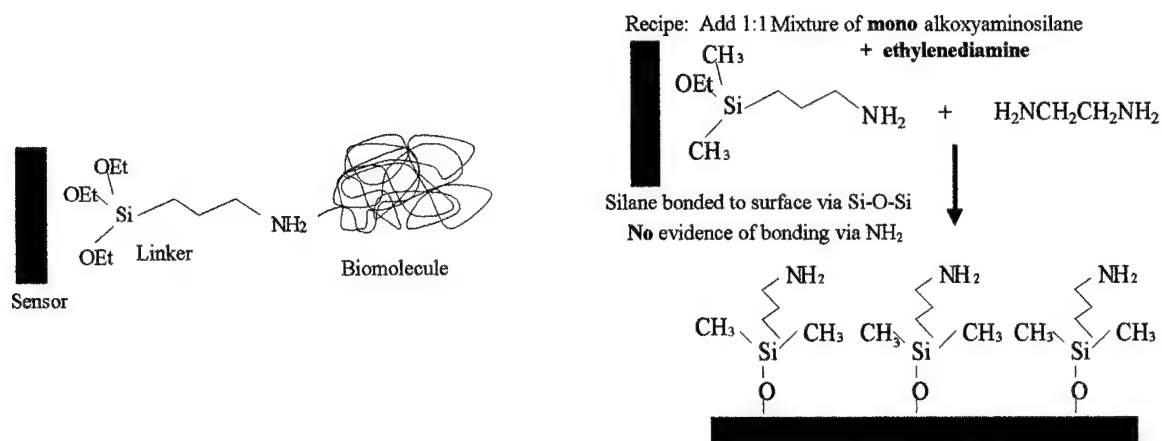


Fig.32 Silane treatment of the sensor surface provides well defined amine groups (NH₂) which provide binding sites for biomolecules.

3.4 Molecular Beacon and Padlock Probes

This research was directed towards novel methods for specific nucleic acid detection and identification. The strategy is to employ more specific, isothermal non-PCR molecular amplification methods. Using highly specific fluorescent probes including molecular padlocks and molecular beacons (Fig.33), we have determined the optimal parameters for isothermal molecular amplification and identification, which is an important step towards a complete simple and sensitive diagnostic test for identification of bacterial and viral pathogens. The systems that were characterized include three phylogenetically distant organisms: *Renibacterium salmoninarum* (BKD, bacterium), *Bacillus cereus* (BCER, bacterium), and infectious hematopoietic necrosis virus (IHNV, virus). Accomplishments include (i) production of fluorescent species-specific probes (ii) design and testing of circularizable nucleic acid probes for amplification of fluorescent probe targets and (iii) attainment of target amplification (by rolling circle replication) in excess of 1 million-fold at room temperature in two hours.

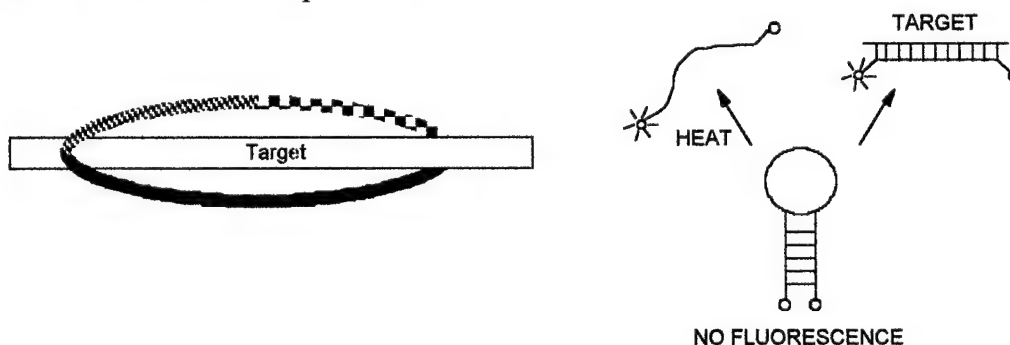


Fig.33 Schematic diagram of a padlock probe (left) and detection of sequence-specific nucleic acid targets using molecular beacons (right). The hatched and checked segments of the probe (left) represent the ends of the linear padlock probe that hybridize to the target sequence and are connected by the linker shown in black. In the presence of a target sequence complementary to the loop portion of the molecular beacon (right), the base-paired stem structure of the beacon dissociates and a fluorescent signal is produced.

4. INFRASTRUCTURE AND INSTRUMENTATION

Several critical pieces of equipment were acquired under this project; this equipment complements existing instrumentation at LASST acquired through other funding sources.

Device Fabrication

Class 1000 clean room including microelectronics grade deionized water system, multi-station wet bench, surface profilometry, wafer rinser/dryer, wafer dicing saw.

Surface Structure / Atomic Scale Imaging

variable temperature scanning probe microscope (SPM) including atomic force microscopy (AFM) and scanning tunneling microscopy (STM).

Spatially Resolved Chemical Composition

X-ray photoelectron spectroscopy (XPS), scanning Auger spectrometer (AES), ion gun depth profiling

Electronic Characterization

impedence spectrometer

Molecular Adsorption Characterization

infra-red spectrometer

Gas Phase Reactant / Product Distributions and Sensor Response

8-channel gas delivery system, gas chromatograph / mass spectrometer, data processing hardware and software, heater control circuitry, mixing and calibration of gas bottles

5. RESEARCH PUBLICATIONS AND PRESENTATIONS

Publications

- "Chemical Modification of Metal Oxide Surfaces in Supercritical CO₂: The Reaction of Chlorosilanes with Silica," J. C. Combes, L. D. White and C. P. Tripp, *Langmuir* **15**, 7870 (1999).
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- "Implications of the reactivity of methanol and dimethyl methylphosphonate for sensing mechanisms of tungsten oxide-based sensors" Rebekah S. Pilling, *Honors thesis in Chemistry* (May 2000).
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- “In-situ Structural, Chemical and Electrical Characterization of WO₃ Sensor Films,” S.A. Ding, Chung Kim, and R.J. Lad, 46th National Symposium of the American Vacuum Society, Seattle, WA, October 1999 (poster)
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- “Reaction of NO on WO₃ Powders,” J. Cox and C. Tripp, ACS Meeting, April, 2000.

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- “Novel Bulk Acoustic Wave Sensors for Probing Liquid Electrical Property Changes,” C. Zhang, R.B. Haskell, T. Grillo, J. Seitz, J.F. Vetelino, and F.G. Grillo, 198th Meeting of The Electrochemical Society, Phoenix, AZ, October 22-27, 2000 (talk)
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- “Ultra-thin Tungsten Oxide Based Films for Chemical Sensors,” R.J. Lad, Spring 2001 Meeting of the European Materials Research Society, Strasbourg, France, June 7, 2001 (invited talk)
- “Electronic Transport Mechanisms in WO₃-Based Ultra-thin Film Chemiresistive Sensors,” S.C. Moulzolf and R.J. Lad, The 11th International Conference on Solid-State Sensors and Actuators, Transducers '01, Eurosensors XV, Munich, Germany, June 14, 2001 (talk).
- “Charge Transport Mechanisms in Epitaxial Tungsten Oxide Films Used for Chemiresistive Sensors,” S.C. Moulzolf and R.J. Lad, 48th International Symposium of the American Vacuum Society, San Francisco, CA, Oct. 29, 2001 (talk)
- “Growth and Structure of Ultrathin Silver and Silver Oxide Films on Sapphire Surfaces,” F.X. Bock, S. Rivers, and R.J. Lad, 48th International Symposium of the American Vacuum Society, San Francisco, CA, Oct. 30, 2001 (talk)
- “In-Situ Conductivity and Hall Effect Characterization of Tungsten Oxide Thin Films,” S.C. Moulzolf, D.J. Frankel, and R.J. Lad, 2001 Fall Meeting of the Materials Research Society, Boston, MA, Nov. 28, 2001 (talk)
- “Microsensor Research at UMaine,” J.F. Vetelino, Univ of Brescia, National Institute of Physics and Materials, Brescia, Italy, July 6, 2000.
- “Microsensor Research at UMaine,” J.F. Vetelino, Univ. of L'Aquila, Dept. of Chemistry, Chemical Engineering and Materials, L'Aquila, Italy, July 11, 2000.
- “Novel Electrode Configurations of Bulk Acoustic Wave Resonators for Liquid Sensing Applications,” J.F. Vetelino, 2000 IEEE Ultrasonics Symposium, Puerto Rico, Oct. 22-25, 2000.
- “The Bleustein-Gulyaev Wave Mode in Potassium Niobate for Liquid Sensing Applications,” J.F. Vetelino, 2000 IEEE Ultrasonics Symposium, Puerto Rico, Oct. 22-25, 2000.

- “Theoretical Investigation of Bleustein-Gulyaev Waves in Potassium Niobate for Liquid Sensing Applications,” C. Zhang and J.F. Vetelino, 198th Electrochemical Society Meeting, Phoenix, Arizona, October 21, 2000.
- “Novel Bulk Acoustic Wave Sensors for Probing Liquid Electrical Property Changes,” C. Zhang and J.F. Vetelino, 198th Electrochemical Society Meeting, Phoenix, Arizona, October 21, 2000.
- “Bulk Acoustic Wave Modes in Quartz for Sensing Measurand-induced Mechanical and Electrical Property Changes,” C. Zhang and J.F. Vetelino, 198th Electrochemical Society Meeting, Phoenix, Arizona, October 21, 2000.